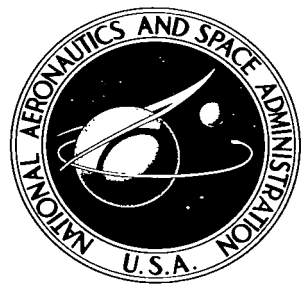
NASA TECHNICAL TRANSLATION

NASA TT F-417



NASA TT F-417

c. 1

TECH LIBRARY KAFB, NM
0068849

LOAN COPY: RETUR
AFWL (WLIL-2)
KIRTLAND AFB, N

EXTRACTION OF METAL COMPOUNDS FROM PYRAZOLINE DITHIOCARBAMINATES

by V. M. Byr'ko

From *Trudy Komissii po Analiticheskoy Khimii,*
Vol. 14, 1963

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION - WASHINGTON, D. C. - MAY 1966

TECH LIBRARY KAFB, NM
0068849

EXTRACTION OF METAL COMPOUNDS FROM PYRAZOLINE DITHIOCARBAMINATES

By V. M. Byr'ko

Translation of "Ekstraktsiya soyedineniy metallov s pirazolinditiokarbaminatami."
Trudy Komissii po Analiticheskoy Khimii,
Vol. 14, pp. 191-201, 1963

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – Price $1.00

EXTRACTION OF METAL COMPOUNDS FROM PYRAZOLINE DITHIOCARBAMINATES

V. M. Byr'ko

ABSTRACT

Metal dithiocarbaminates are extracted from an acid medium; the degree of extraction and the necessary range of acidity are determined by the tendency of the given metal to form stable compounds with reagents containing sulfur and by the rate at which these compounds are formed, and not by the rate at which the reagent is decomposed by acids. A strong variation in the anion concentration of the reagent when the acidity is increased may result in the appearance of minima on the extraction curves. The minima which appear on the extraction curves for pyrazoline dithiocarbaminates of metals which have several valence states are caused in many instances by a change in the redox potentials. Minima may also appear on extraction curves when there is a change in the ion state of the elements in solution.

Salts of dithiocarbamic acids are very important in analytic chemistry. /191* About one hundred derivatives of dithiocarbamic acids are presently known (a considerably smaller number have been studied in detail), and this number will apparently be increased as disulfates and carbaminates are prepared from amines with weakly basic properties (aromatic amines, pyrazoles). Reviews of the literature contain incomplete or obsolescent material on the analytic application of dithiocarbaminates (refs. 1-3).

Dithiocarbaminates form highly extractable chelate compounds with metal ions. It is generally known that the anion forms of the reagent molecules react during the formation of chelate compounds (ref. 4). The fraction of reagent capable of reacting with metal ions varies strongly with a change in acidity, depending on the type of reagent used (amphoteric compound, mono- or dibasic acid). This determines the extraction range and the shape of the extraction curves. Some interesting facts can be derived from a calculation of the variation in the concentration of anions and molecules of dibasic acids in aqueous solutions of their alkaline salts with a change in hydrogen concentration.

---

*Numbers given in margin indicate pagination in original foreign text.

We shall assume that dithiocarbaminates are weak monobasic acids with dissociation constant K_1 which are decomposed by a mineral acid. A monomolecular mechanism is responsible for the decomposition reaction (refs. 5-7), which takes place with a constant K_2. For the case of a constant infinitely small time interval, assuming that equilibrium in the system is reached in a period which is less than the selected time, the following process will take place.

Hydrolysis takes place in aqueous solutions of salts of weak monobasic acids and strong bases. If the concentration of an alkali salt of dithiocarbamic acid is much less than K_1 for this acid, then at values of $pH \geq pK_1 + 2$ the salt is almost completely dissociated, and the anion concentration of /192 the dithiocarbaminate is equal to the salt concentration. In this case, there will be a moles of the R^- anion of dithiocarbamic acid. There will be almost no undissociated HR molecules or decomposition products. When the concentration of mineral acid in the solution is increased, x moles of the R^- anion are converted to dithiocarbamic acid HR, which takes on a betaine structure and decays into carbon disulfide and amine. We designate the number of moles of acid subjected to decay by the letter y. The number of undissociated acid molecules will be x - y, the number of unbound R^- anions is equal to a - x. The change in the number of R^- anions is described by the equation

$$\frac{dx}{d[H^+]} = K_1(a - x). \tag{1}$$

The number of moles of HR subjected to decay is determined by the expression

$$\frac{dy}{d[H^+]} = K_2(x - y). \tag{2}$$

Integrating (1) within limits from 0 to $[H^+]$ (ref. 8), we get the number of anions

$$R^- = a - x = ae^{-K_1[H^+]}; \tag{3}$$

$$x = a(1 - e^{-K_1[H^+]}). \tag{4}$$

Substituting equation (4) in expression (2), we get

$$\frac{dy}{d[H^+]} + K_2 y = K_2 a(1 - e^{-K_1[H^+]}) \tag{5}$$

and integration gives

$$y = \left(1 - \frac{K_2}{K_2 - K_1} e^{-K_1[H^+]} + \frac{K_1}{K_2 + K_1} e^{-K_2[H^+]}\right). \quad (6)$$

Subtracting (6) from (5), we get the quantity of HR as a function of acidity

$$x - y = \frac{K_1 a}{K_2 - K_1} (e^{-K_1[H^+]} - e^{-K_2[H^+]}). \quad (7)$$

These functions are known; graphs are given for them in figure 1. We are not interested in the amount of the decay products (6).

The concentration of the reagent anions changes rapidly with a change in acidity (fig. 1, curve 1), and in an actual system which also contains metal ions, equilibrium is not established instantaneously. This means that /193 anomalous minima and maxima may be expected on the extraction curves, particularly during extraction of metals which form stable compounds in different valence states with dithiocarbaminates, since dithiocarbamic acids have reduction properties. Obviously the reduction capacity of the reagents will vary greatly with a change in the concentration of hydrogen ions, since the change in dithiocarbamic acid concentration is just as great in this case, passing through a maximum (fig. 1, curve 2). If consideration is given to the fact that the state of the metal ions and structure of the reagents may also change in this case, and that all interactions between metal ions and reagents take place against a background of concurrent reactions between metal ions and components of the aqueous phase (OH^-, masking substances, etc.), then the minima and maxima which appear on the extraction curves may be assumed to be more of a regular rule than they are a special case.

Although the anion concentration of the reagent is considerably reduced when the acidity of the solution is increased, calculations show that when a solution of a reagent with $K_1 = 10^{-7}$ and concentration of 10^{-1} mole/l is held in

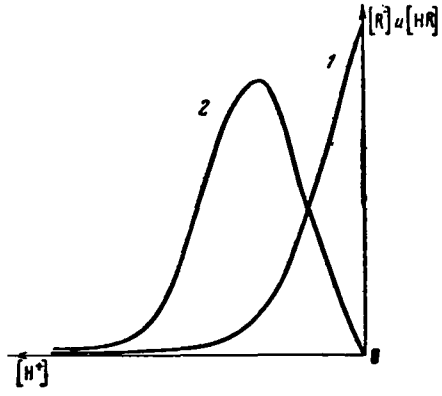


Figure 1. Concentration of R^- (1) and HR (2) as a function of hydrogen ion concentration.

a 5 N acid for 10 sec, the anion concentration in the aqueous phase is $2 \cdot 10^{-9}$ mole/l. This means that when the metal concentration is 10^{-5} mole/l, all bivalent ions are precipitated whose concentration product in the aqueous phase exceeds the solubility product of MeR_2 (10^{-23}). Consequently, these ions may be extracted.

Thus, the extraction ranges for compounds of metals with dithiocarbaminates are determined first of all by the tendency of the given metal to form a stable compound with the given reagent, and also by the rate of formation of the compound, and not by the rate at which the reagent is decomposed by acids. Experimental data are given in references 9-11 which confirm these hypotheses for extraction of metal compounds with sodium diethyl dithiocarbaminate in an /194 acid medium. The case of pyrazoline dithiocarbaminate will be discussed below.

In this paper, the extraction of metal compounds with monoderivatives of Δ^2-pyrazoline dithiocarbaminates (PDTC) is studied as a function of the acidity of the medium. In comparison with the widely used diethyl dithiocarbaminates, the pyrazoline dithiocarbaminates of metals have a very intense pigmentation. This apparently is due not only to the presence of chromophores, but also to the possibility of conjugation of the ethylene bond of the pyrazoline ring with π-electrons of the substituent in position 3, i.e., conjugation in a 1-3 system. Pyrazoline dithiocarbaminates are decomposed by acids. In addition, they are comparatively easily oxidized due to the sulfohydryl group (e.g., by iodine, H_2O_2, etc.) forming the corresponding disulfides.

Metals of the hydrogen sulfide and ammonium sulfide group may be divided into several classes according to the nature of the interaction with pyrazoline dithiocarbaminates, depending on the electrostatic characteristics (ref. 12), solubility product of the corresponding sulfide, redox potentials, complex-forming ability, and other properties.

Extraction of several elements in groups I, II, III, VI and VII of the periodic table was studied. Experiments were conducted with the corresponding radioactive isotopes (concentration 10^{-5} - 10^{-6} mole/l). The usual methods and equipment were used for measuring radioactivity. The volume ratio for the aqueous and organic phases was set equal to 1:1. HCl and NaOH were used for acidity. Ordinary buffer mixtures were used in the pH range from 1-13. A previously described method (ref. 13) was used for preparing the pyrazoline dithiocarbaminates. If not specifically stipulated, the reagent concentration in each experiment corresponds to the stoichiometric ratio with respect to the highest valence of the metal. Chloroform was used as the solvent.

Extraction of Copper, Cadmium, Zinc, Gallium, and Thallium

Extraction curves for these elements are given in figure 2. As may be seen from this figure, compounds of copper with 5-phenyl pyrazoline dithiocarbaminate

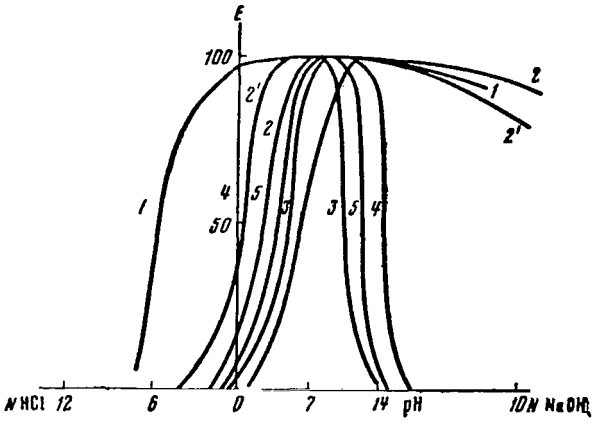


Figure 2. Percent extraction E for Cu (1), Tl^{I} (2), Tl^{III} (2'), Ga (3), Cd (4), and Zn (5) in the form of compounds with 5-phenyl pyrazoline dithiocarbaminate as a function of acidity.

(other PDTC's give similar curves) are extracted over a wide range of acidities. This confirms our hypotheses, since we did not take an excess of reagent.

Thallium (Tl^{I} and Tl^{III}) is extracted from strongly alkaline solutions, and in these conditions may be separated from nearly all elements. Minima are observed in the case of Cu^{II}, Tl^{I} and Tl^{III} due to the rapid change in reagent concentration; it is obvious that the composition of buffer mixtures, /195 presence of masking substances, etc. are also important.

Since all compounds of metals with this group (except copper) absorb in the near ultraviolet range, the best method for determination of these elements is the radiometric method with respect to exchange, using the stability series for pyrazoline dithiocarbaminates (ref. 14).

Molybdenum Extraction

Molybdenum belongs to that class of elements which easily form aggregates in aqueous solutions due to polymerization reactions determined by the pH of the solution and the concentration of the element.

Like diethyl dithiocarbaminate, pyrazoline dithiocarbaminate also forms red and yellow compounds with molybdenum. The yellow compound is formed when the dithiocarbaminate is added to a neutral or weak acid solution of hexavalent molybdenum. This changes in time to the red compound. The speed of this transition varies for different dithiocarbaminates, apparently depending on the redox potential of the reagent and on the acidity of the solution, i.e., what

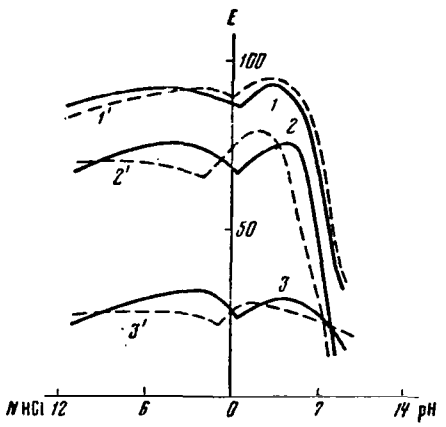


Figure 3. Percent extraction E for Mo^{V} and Mo^{VI} with various dithiocarbaminates as a function of acidity: 1, Mo^{VI} with diethyl dithiocarbaminate; 2, Mo^{VI} with 5-phenyl pyrazoline dithiocarbaminate; 3, Mo^{VI} with 3,5-phenyl pyrazoline dithiocarbaminate; 1', 2', 3', the same reagents with Mo^{V}.

takes place is probably reduction of the molybdenum to the pentavalent form by the reagent. Pentavalent molybdenum forms the red compound. Disulfides do not interact with either Mo^{VI} or Mo^{V}.

Radiometric analysis showed that the molar concentration of reagent /196 to molybdenum is 2:1 for both valence states.

Mo^{VI} and Mo^{V} extraction curves are shown in figure 3 for various pyrazoline dithiocarbaminates. Minima in the 0-1 pH region correspond to the isoelectric point where paramolybdate anions are converted to the polymerized molybdenyl cation. Hydrated molybdenum trioxide settles out at this point (MoO_2^{2+} is then converted to the polymerized cation).

In addition to reagent concentration, complex formation and pH value have a strong effect on the equilibrium of this redox system. Appropriate conditions were chosen for one reagent (5-phenyl pyrazoline dithiocarbaminate) so that both the yellow and red forms were stable. This was done by adding sodium tartrate (fig. 4). It was found that the yellow form is extracted from an acid medium, while a weak acid medium produces the red form. Concurrent formation

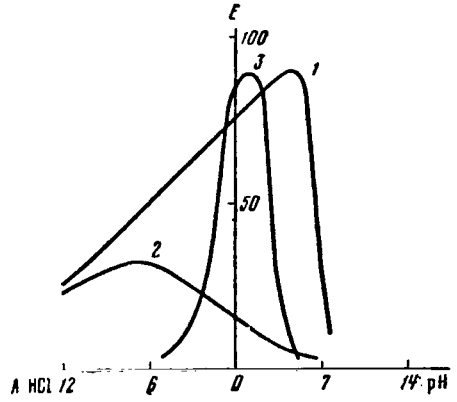


Figure 4. Percent extraction E for compounds of molybdenum and tungsten with 5-phenyl pyrazoline dithiocarbaminate in the presence of sodium tartrate as a function of acidity: 1, Mo^{V}; 2, Mo^{VI}; 3, W^{VI}.

of Mo^{VI} and Mo^{V} compounds with PDTC as well as the corresponding compounds of tartrate complexes have an important effect in this case.

The extraction of W^{VI} in the presence of these same quantities of /197 reagent is shown in figure 4. Tungsten extraction is reduced by the addition of sodium tartrate. The practical conclusion from this is that molybdenum may be easily separated from tungsten in the presence of sodium tartrate at a pH of 3.5-4.

Photometric extraction may also be used for determination of molybdenum in the presence of tungsten. We have developed a method on this basis for determination of molybdenum in tungsten salts and concentrates (ref. 15).

Extraction of Niobium and Tantalum

Interaction between niobium and diethyl dithiocarbaminates is mentioned in several works (refs. 16-19). Extractable compounds are formed. Extraction was done from solutions prepared by melting Nb_2O_5 and Ta_2O_5 containing the appropriate radioactive isotopes with ammonium pyrosulfate. A 3 percent solution of tartaric acid was used for lixiviation.

Our experiments show that a large excess of dithiocarbaminate is needed for niobium extraction. We always took 1000 times the quantity of reagent (in moles) to guarantee comparable results. The curves plotted from this experiment are shown in figure 5. The niobium extraction is excellent. The amount of tantalum extracted under these conditions reaches 10-15 percent. /198

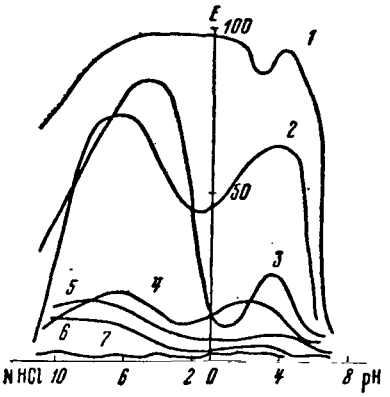


Figure 5. Percent extraction E for compounds of niobium and tantalum with various dithiocarbaminates and diethylamine as a function of acidity: 1, Nb with hexamethylene dithiocarbaminate; 2, Nb with diethyl dithiocarbaminate; 3, Nb with 5-phenyl pyrazoline dithiocarbaminate; 4, Ta with diethyl dithiocarbaminate; 5, Ta with diethylamine; 6, Nb with 5-furyl-3-phenyl pyrazoline dithiocarbaminate; 7, Nb with 3,5-diphenyl pyrazoline dithiocarbaminate.

The quantity of niobium and tantalum extracted by 3,5-diphenyl and 3,5-furylphenyl derivatives is negligible at any ratios of reagent and element (fig. 5, curves 6 and 7). In the interval from pH 3 to 2 N HCl, an extractability minimum is observed for extraction of niobium by several reagents from tartaric solutions (fig. 5, curves 1, 2 and 3). The nature of the extraction curves does not change with other extractants (ethyl acetate, α-naphthylamine).

We assumed that the extractability of niobium and tantalum is associated with the appearance of the corresponding amines due to dissolution of the reagents in acid solutions. These elements were extracted in the presence of the initial amines dissolved in chloroform. The molar quantities of the amines were the same as when the corresponding dithiocarbaminates were used for extraction. It was found that niobium is extracted only slightly by all amines, and the extraction of tantalum is approximately the same as in the case of the corresponding carbaminates. It may be assumed that the amines formed /199 during dissolution of the reagents participate to a certain extent in the extraction of tantalum; reaction with dithiocarbaminates or some types of compounds formed when they are interacted with acids is apparently more characteristic for niobium.

We attempted on the basis of our data to separate tantalum and niobium by extracting compounds of niobium with hexamethylene dithiocarbaminate, diethyl dithiocarbaminate and 5-phenyl pyrazoline dithiocarbaminate at pH 5 and in 5 N HCl. However, nothing positive was obtained at any element ratios. The amount of niobium extracted falls sharply for all three reagents in the presence of tantalum. When niobium alone is extracted by these reagents, 97 percent recovery may be reached.

Rhenium Extraction

Interaction between dithiocarbaminates and rhenium has been studied very little. For instance, Yu. A. Chernikhov and B. M. Dobkina (ref. 9) note that the compound formed during interaction of perrhenate with diethyl dithiocarbaminate in 10-12 N HCl may be extracted by ethyl acetate. However, Bode (ref. 16) is dubious about this and believes that perrhenate does not interact /200 with diethyl dithiocarbaminate, and that the results of Yu. A. Chernikhov and B. M. Dobkina may be explained by the possible extraction of perrhenate by an ester.

We studied extraction of perrhenate with diethyl dithiocarbaminate and pyrazoline dithiocarbaminate (fig. 6). Perrhenate is also extracted by disulfides, and not by the initial amines dissolved in the chloroform. Re^{V} prepared by reduction of bismuth amalgam according to A. I. Lazarev's method (ref. 20), and Re^{III} were extracted by PDTC within a wide range of acidities. Re^{IV} and Re^{V} are extracted by 3,5-diphenyl disulfide. Re^{III} and Re^{V} are extracted quite well from sulfuric acid solutions by diethylamine and other amines.

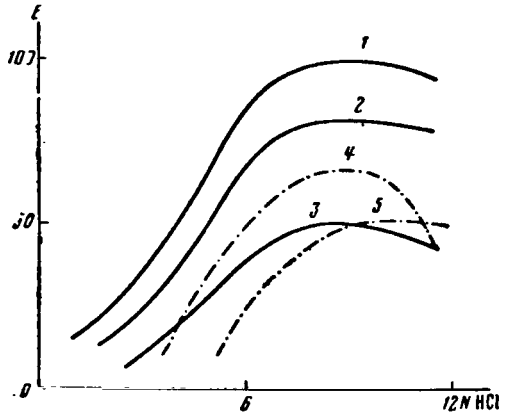


Figure 6. Percent extraction E for compounds of rhenium with various pyrazoline dithiocarbaminates: 1, Re^{VII} with diethyl dithiocarbaminate; 2, Re^{VII} with 5-phenyl pyrazoline dithiocarbaminate; 3, Re^{VII} with 3,5-diphenyl pyrazoline dithiocarbaminate; 4, Re^{IV} with 3,5-diphenyl pyrazoline dithiocarbaminate disulfide; 5, Re^{V} with 3,5-diphenyl pyrazoline dithiocarbaminate disulfide.

Re^{IV} prepared by reduction using hydrazine (ref. 21) is not extracted by amines and carbaminates since the $ReCl_6^{2-}$ complex is apparently quite stable. However, the corresponding disulfides interact weakly with Re^{IV}; 3,5-diphenyl pyrazoline disulfide reacts better than the others (fig. 6).

The $Re^{VII} \rightarrow Re^{V} \rightarrow Re^{IV} \rightarrow Re^{III}$ reduction is not very probable, although the hydrazine disulfide precipitating out during decomposition may emerge as a reducing agent. The dithiocarbaminate is apparently more stable.

These data have been used as a basis for development of a photometric extraction method for determination of Re^{IV} in the presence of Mo, W, U and other elements, since these elements do not interact with disulfide.

REFERENCES

1. Zahradnik, R. Chem. Tech., Berlin, 10, 546, 1959.

2. Podchaynova, V. N. Transactions of the Analytical Chemistry Commission, Trudy Komissii po analit. khimii, 11, 146, 1960.

3. Whelcher, V. Organic Analytical Reagents, Van Nostrand, Toronto-New York-London, Vol. 4, p. 77, 1948.

4. Morrison, J. and Freyzer, G. Extraction in Analytical Chemistry (Ekstraktsiya v analiticheskoy khimii). Goskhimizdat, Moscow-Leningrad, p. 30, 1960.

5. Zahradnik, R. and Zuman, P. Collection, 24, 432, 1952.

6. --- Chem. listy, 52, 231, 1958.

7. Zuman, P. and Zahradnik, R. Z. phys. Chem., 208, 135, 1957.

8. Rakovskiy, A. V. Chemical Kinetics and Analysis (Khimicheskaya kinetika i analiz). ONTI, Moscow, p. 9, 1931.

9. Chernikhov, Yu. A. and Dobkina, M. V. Zav. lab., 15, 1143, 1949.

10. Malissa, H. and Gomisček, S. Rudarsko-met. zbornik, No. 1, 17-20, 1959.

11. --- Z. anal. chem., 169, 401-404, 1959.

12. Yatsimirskiy, K. B. Zh. analit. khimii, 9, 282, 1954.

13. Kost, A. N., Busev, A. I., Grandberg, I. I. and Byr'ko, V. M. Nauchnyye doklady vysshey shkoly. Khimiya i khim. tekhnologiya, No. 2, 349, 1958.

14. Busev, A. I. and Byr'ko, V. M. Vestn. Mosk. gos. un-ta, No. 3, 46, 1960.

15. Busev, A. I. and Byr'ko, V. M. Vestn. Mosk. gos. un-ta, No. 2, 76, 1960.

16. Bode, H. Z. anal. Chem., 144, 165, 1959.

17. Tserkovnitskaya, I. A. and Borovaya, N. S. Uch. zap. Leningradsk. un-ta, Issue 19, No. 297, 96, 1960.

18. Malissa, H. Mikrochim. acta, 1953, 726.

19. Tyutina, N. A., Aleskovskiy, V. B. and Miller, A. D. Trudy Leningradsk. tekhnologich. in-ta im. Lensoveta, Issue 10, 101, 1958.

20. Lazarev, A. I. Zh. neorgan. khimii, 1, 385, 1956.

21. Meyer, R. J. and Rulfe, Ch. Z. Anal. Chem., 27, 1387, 1955.

Translated for the National Aeronautics and Space Administration
by John F. Holman and Co. Inc.

NASA-Langley, 1966 F-417

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546